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Vibrational spectra and normal coordinate calculations of para chloro benzoic acid

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Abstract : The FTIR and laser Raman spectra of para chloro benzoic acid have been recorded in the regions 200-4000 cm^{-1} and 30–4000 cm^{-1} using Shimadzu FTIR 8101 spectrophotometer and carry model 82 grating spectrophotometer respectively The vibrational analysis has been carried out by assuming C_s symmetry. The observed frequencies were assigned to various modes of vibrations on the basis of intensity, frequencies from allied molecules and the normal coordinate calculations. The potential energy distribution associated with normal modes are also reported here The assignment of fundamental vibrational frequencies for para chloro benzoic acid agree well with the calculated frequencies

Keywords : Vibrational spectra, normal coordinate calculation, para chloro benzoic acid

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1. Introduction

The present study is a part of our on going discussions on the vibrational spectra of the derivatives of benzoic acid. The derivatives of benzoic acid are widely used in several applications such as miticides, contrast media in urology, cholocystographic examinations and in the manufacture of pharmaceuticals. It also finds application in dyes, in curing tobacco, in preserving fruits juice, in many esters, as a mordant in cloth printing and as a reference standard in volumetric analysis. Vibrational spectra of benzoic acid and substituted benzoic acids have been studied by various workers [1–3]. Rastogi *et al* [1] have reported about the vibrational study of 3,5–dinitrobenzoic acid. However, there is no report on the vibrational spectra of para chloro benzoic acid in the literature. Hence, an attempt has been made in the present work to record the FTIR and laser Raman spectra of para chloro benzoic acid and to study the complete vibrational analysis on the basis of C_s point group.

2. Experimental details

Pure chemical, para chloro benzoic acid, white solid powder was obtained in the solid form, from SISCO–CHEM Industries, Bombay. The FTIR spectrum was recorded in the region

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200–4000 cm^{-1} on Shimadzu FTIR 8101 spectrophotometer in KBr, the IR spectrum was recorded in the region 600–4000 cm^{-1} on Perkin–Elmer IR 983 and the laser Raman spectrum was recorded in the region 30–4000 cm^{-1} on Carry Model 82 grating spectrophotometer the 488 nm radiation from an argon ion laser operating at 4 W was used for excitation. The spectral width was 2 cm^{-1} and the scanning speed was 30 cm^{-1} min^{-1}. The frequencies for all sharp bands are accurate to ±1 cm^{-1}.

3. Normal coordinate treatment

The calculation of normal vibration was made by the method of Wilson [4]. The potential energy was expressed by a simplified general valence force field (SGVFF) for the following reasons : (i) SGVFF has been shown to be very effective in normal co-ordinate analysis of benzene derivatives. (ii) Valence force constants can be transferred between the related molecules which is very useful in normal co-ordinate analysis [5].

The structural parameters employed in this work were taken from Mohan and Ravikumar [6]. The normal co-ordinate calculations were performed using the modified schachtschneider programme [7]. The initial set of the valence force constants and the corresponding off-diagonal constants were transferred from related benzene derivatives reported recently [5,8]. A zero order calculation with the transferred force constants was performed and the result showed a reasonable agreement between the calculated and observed frequencies for most of the normal modes, except for the low frequency skeletal modes Hence, the initial set of force constants were refined by least square technique in accordance with the position of bands in the infrared and Raman spectra. The final set of the refined force constants are shown in Table 1.

Table 1. Final set of force constants of para chloro benzoic acid (in units of m dyne A^{-1} Rad^{-1} and m dyne A^{-1} Rad^{-2}).

Types of constants		Parameter	Coordinates involved	Final
Diagonal constants	Stretching	f_d	H C	4 5
		f_D	C C	3.8
		f_l	C C	2 8
		f_q	C C	3.9
		f_n	C C	4.6
		f_s	C C	3.6
		f_r	C C	4 1
		f_p	C C	3.6
		f_m	C Cl	3.7
	Bending	f_α	H $\hat{C}$C	0.28
		f_γ	C $\hat{C}$C	0.8
		$f\phi$	C $\hat{C}$C	1.0
		f_θ	C $\hat{C}$Cl	1.0

Table 1. *(Contd.)*

Types of constants		Parameter	Coordinates involved	Final
		$f\delta$	C $\hat{C}$ Cl	0.51
		f_β	C $\hat{C}$C	1.0
Interaction constants	Stretch-stretch	f_{dD}	HC CC	0.19
		f_{Dq}	CC CC	0.06
		f_{qn}	CC CC	0.08
		f_{sm}	CC CCl	0.28
	Stretch-bend	$f_{d\alpha}$	HC H $\hat{C}$C	0.25
		$f_{D\gamma}$	CC C $\hat{C}$C	0.36
		$f_{q\gamma}$	CC C $\hat{C}$C	0.34
		$f_{m\delta}$	CCl C $\hat{C}$ Cl	0.11
		$f_{n\phi}$	CC C $\hat{C}$C	0.41
		$f_{p\theta}$	CC C $\hat{C}$C	0.41
		$f_{d\theta}$	CH C $\hat{C}$C	0.33
	Bend-bend	$f_{\gamma\phi}$	C $\hat{C}$C C $\hat{C}$C	0.14
		$f_{\alpha\gamma}$	H $\hat{C}$C C $\hat{C}$C	0.12
		$f_{\beta\delta}$	C $\hat{C}$C C $\hat{C}$ Cl	0.28
		$f_{\gamma\theta}$	C $\hat{C}$C C $\hat{C}$C	0.13

4. Results and discussion

The observed frequencies with their relative intensities and assignments of para chloro benzoic acid are given in the Table 2. This compound belongs to C_s point group. In this point

Table 2. Observed and calculated frequencies (cm^{-1}) and potential energy distribution for para chloro benzoic acid

Species	Observed frequencies and intensity			Calculated frequency	Assignments/*P.E.D.*
	IR	FTIR	LR		
	3940 W				3090+850
	3879 W				3060+820
	3822 W		3835 W		2×1597+640
	3620 M				2938+680
	3490 M				2×1270+955
	3475 M				O–H stretching*
	3105 M			3101	C–H stretching 92
	3090 M	3090W	3080 M	3086	C–H stretching 94
	3060 M	3050 W		3058	C–H stretching 95
	2938 M			2928	C–H stretching-88
			2700 W		2×1186+320
	1748 W				2×1200–642
	1698 M				C=O stretching*
	1684 M	1680 S		1675	C=C stretching 91

Table 2. *(Contd.)*

Species	Observed frequencies and intensity			Calculated frequency	Assignments/*P.E.D.*
	IR	FTIR	LR		
	1652 M				3105 – 2× 725
a′			1628 M	1619	C=C stretching 87
a′		1590 S	1597 S	1586	C=C stretching 94
a′	1575 M	1573 W			1095 + 472
	1495 W	1492 W			1175 + 325
	1435 W	1429 M			O–H in–plane bending*
a′			1358 W	1351	C–C stretching 82
		1295 W	1299 W		C–O stretching*
a	1270 M	1282 W		1272	C–C stretching 79
a	1200 M			1186	C–C stretching 81
a′		1175 M	1186 M	1169	C–COOH stretching 56
a′		1130 M	1143 M	1128	C–H in-plane bending 48
a′		1095VS	1105 M	1087	C–H in-plane bending 55
a′	1041 W			1030	C–H in-plane bending 61
a′	1013 W	1013 S		1005	C–H in-plane bending 65
a′	989 M			974	C–H out-of-plane bending 58
a′	955 M			945	C–H out-of-plane bending 51
a′	850 M	855 S		842	C–H out-of-plane bending 42
a′	820 M		815 S	819	C–H out-of plane bending 49
	810 M	810 W	800 VW		O–H out-of-plane bending*
		762 VS	750 M		O–C–O in-plane bending*
	732 M				C=O out–of -plane bending*
a′	725 M	725 W		714	C–Cl stretching 72
a″	680 Vs	685 S		681	C–C–C out–of–plane bending 65
a	642 W	630 W	640 S	626	C–C–C in-plane bending 70
	628 VS				C–C–O rocking*
a′		549 S		536	C–C–C out-of-plane bending 49
		520 M	520 VW		855 – 332
a		472 S	480 VW	471	C–C–C in-plane bending 52
		352 M	353 M		C–OH in–plane bending*
a′		342 W		328	C–Cl in-plane bending 39
a′		332 W		317	C–COOH in-plane bending 50
a		325 W	320 W	309	C–C–C in-plane bending 54
a″		307 W		301	C–Cl out-of-plane bending 40
		295 M	290 M		1105–815
a″		272 S		265	C–C–C out-of-plane bending 58
		235 M	228 W		C–OH out-of plane bending*
a″		215 S		209	C–COOH out-of-plane bending 39
			108 S		Lattice vibration
			67 VS	—	Lattice vibration

VS – Very strong, VW – Very weak, S – Strong,
MS Medium strong, M – Medium, W – Weak , * Group vibration

group, there are only two types of vibrations, *i.e.*, planar (*a′*) and non-planar (*a″*). They can be distributed as

$\Gamma = 21\ a'$ (planar) $+9\ a''$ (non-planar)

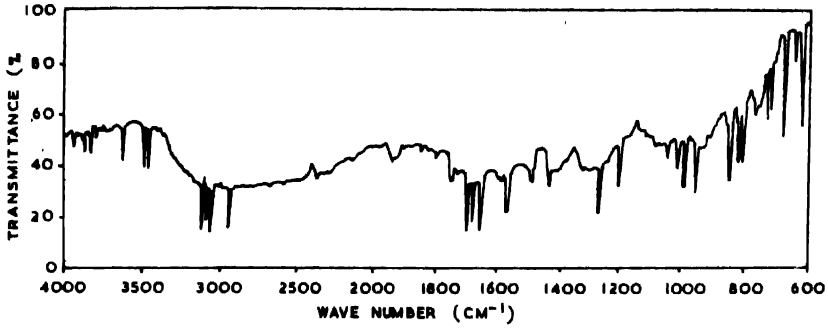

Figure 1. Infrared spectrum of para chloro benzoic acid.

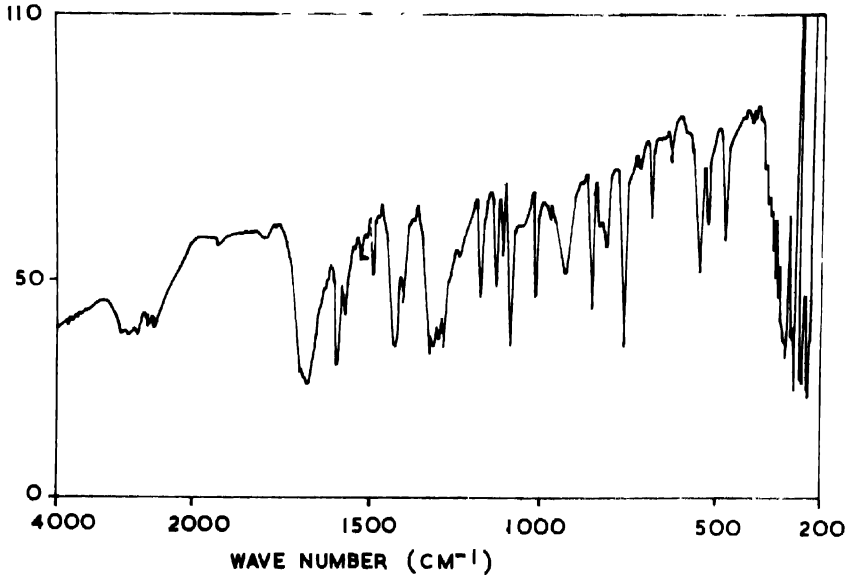

Figure 2. FTIR spectrum of para chloro benzoic acid.

in which a' gives rise to polarised lines whereas a'' gives depolarised lines in the Raman spectrum. All 30 vibrations are active in the IR and Raman spectra. Structure of para chloro benzoic acid and the spectra recorded are shown in the Figures 1–4.

Phenyl ring vibrations

4.1. Carbon vibrations :

The C = C vibrations are more interesting if the double bond is in conjugation with the ring. The actual positions are determined not so much by the nature of substituents but by the form

of substituents around the ring Bellamy 1957 [9]. Benzene has two doubly degenerate modes e_{2g} (1596 cm^{-1}) and e_{12} (1485 cm^{-1}) and two non-degenerate modes b_{2u} (1310 cm^{-1}) and a_{12} (995 cm^{-1}) due to skeletal stretching modes of C–C bonds.

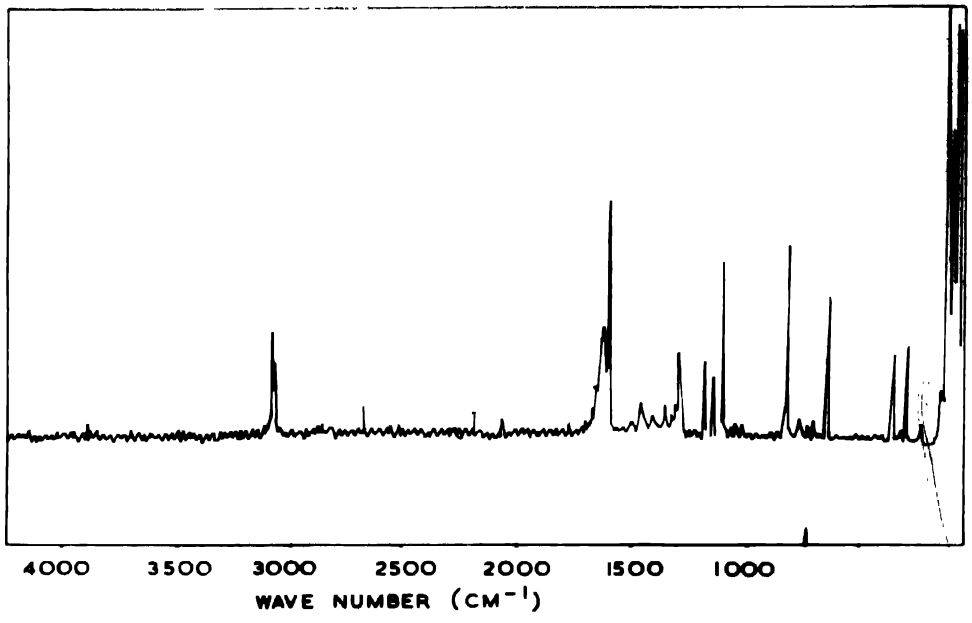

Figure 3. Laser Raman spectrum of para chloro benzoic acid

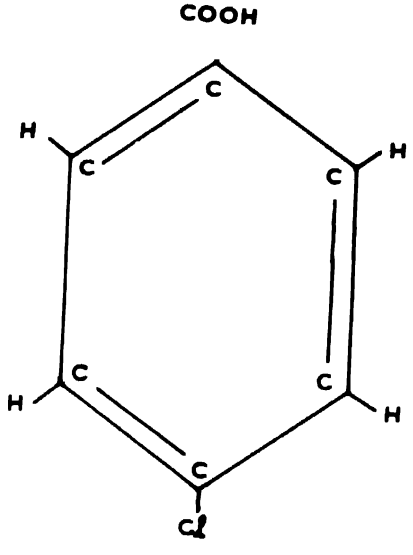

Figure 4. Structure of para chloro benzoic acid

The modes corresponding to C–C stretching in benzene are assigned to the bands at 1680, 1628, 1590, 1358, 1282 and 1200 cm^{-1} in para chloro benzoic acid.

The in-plane carbon bending vibrations, are obtained from the non-degenerate b_{1u} (1010 cm^{-1}) and degenerate e_{2g} (606 cm^{-1}) modes of benzene. The e_{2g} (606 cm^{-1}) degenerate frequency splits into two totally symmetric vibrations under C_s symmetry and they are observed at 630 and 472 cm^{-1} in para chloro benzoic acid.

The carbon out-of-plane bending vibrations are defined by reference to the non-degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene. The former is found to be constant in substituted benzenes and in para chloro benzoic acid it is observed at 685 cm^{-1}. The degenerate e_{2u} (404 cm^{-1}) vibration splits into two non-totally symmetric components and the bands are observed at 549 and 272 cm^{-1}.

4.2. C–H vibrations :

The aromatic structure shows the presence of C–H stretching vibrations in the region 3000–3100 cm^{-1}, C–H in-plane bending in the region 1000–1100 cm^{-1} and C–H out-of-plane bending in the region 800–980 cm^{-1}, which permits ready identification for this structure. In this region the bands are not appreciably affected by the nature of the substituents. The frequencies 3105, 3090, 3060 and 2938 cm^{-1} are assigned for C–H stretching modes in para chloro benzoic acid and these assignments are in good agreement with Augus *et al* 1936 [10], Bailey *et al* 1946 [11]. The frequencies 1130, 1095, 1041 and 1013 cm^{-1} are assigned for C–H in-plane bending and are in favourable agreement with values given in the literatures [12,13]. The frequencies 989, 955, 850 and 820 cm^{-1} are assigned to C–H out-of-plane bending and these assignments are in good agreement with the literature value [14].

4.3. C–Cl vibration :

The C–Cl stretching frequency is generally observed in the region 671–722 cm^{-1}. Hence the strong band at 725 cm^{-1} is assigned to C–Cl stretching frequency. The C–Cl in-plane bending vibration and out-of-plane vibrations are generally observed at 341 cm^{-1} and 306 cm^{-1}. In para chloro benzoic acid the C–Cl in-plane bending vibrations and out-of-plane bending vibrations occur at 342 cm^{-1} and 307 cm^{-1} respectively. The present assignments agree well with the values given in the literatures [15–18].

4.4. C–COOH vibration :

Usually the band around 1185, 330 and 209 cm^{-1} are assigned to C–COOH stretch, C–COOH in-plane bending and to C–COOH out-of-plane bending respectively. In para chloro benzoic acid the assignments are made at 1186 cm^{-1} for C–COOH stretching, 332 cm^{-1} for C-COOH in-plane bending and 215 cm^{-1} for C-COOH out-of-plane bending respectively.

Group vibration

Group vibrations are determined in terms of the motions that the nuclei in a structural group in the molecule undergo during the vibrations and they appear in fairly constant regions in the

4.5. COOH group vibration :

The band observed at 3475 cm^{-1} has its origin in the O–H stretching vibration. The C=O stretching is a characteristic frequency of carboxylic group. The dipole moment derivaties of the COO in-plane bending mode and C=O stretching mode are very large, splitting with marked frequency differences may be expected for these modes and the out-of-phase C=O stretching mode should have a higher frequency than in-phase mode [19]. The band appearing at 1698 cm^{-1} is assigned to C=O stretching vibration. No splitting is observed. OH in-plane bending and C=O stretching vibrations are closely coupled. These are appearing at 1429 cm^{-1} and 1295 cm^{-1} in the present investigation. The bands at 762 cm^{-1} and 628 cm^{-1} are assigned to OCO bending and CCO rocking vibrations. Out-of-plane bending vibration due to O–H give rise to band at 810 cm^{-1}. The out-of-plane bending vibration due to C=O is given as 732 cm^{-1} The OH out-of-plane bending vibration is strongly coupled with C=O out-of-plane bending vibration. The C=O out-of-plane wagging mode of carboxyl group in all likelihood involves motion of both oxygen atoms. The C–OH out-of-plane bending are assigned to frequencies 352 and 235 cm^{-1} respectively. These observation are in close agreement with Ahmad *et al* 1992 [20].

5. Potential energy distribution

To check whether the chosen set of vibrational frequencies contribute maximum to the potential energy distribution, *P.E.D.* has been calculated using the relation,

$$P.E.D. = \frac{F_{ii} L_{ik}^2}{\lambda_k}$$

In the molecule under investigation, the normal modes under symmetry species with comparable magnitudes couple strongly and hence the observed frequencies are the results of mixed modes which is reflected in the potential energy distribution. The highest *P.E.D.* contribution corresponding to each of the observed frequencies are alone listed in the present work. The close agreement between the observed and calculated frequencies confirms the validity of the present assignment.

6. Conclusions

In the present study, a complete vibrational assignment and the analysis of para chloro benzoic acid are available using the frequencies obtained form FTIR and laser Raman spectra on the basis of C_s symmetry.

References

[1] V K Rastogi, Rajpoot and SN Sharma 1984 *Indian J Phys.* **58B** 311 —

[2] Wlodzimierz, Levendowski and Halina Branska 1986 *J Raman Spectrosc* **17** 17

[3] M Pagannone, B Fornari and G Mattei 1987 *Spectrochim Acta* **43A** 1

[4] E B Wilson (Jr.) 1941 *J Chem Phys.* **9** 76

[5] Danuta Michalska 1993 *Spectrochim. Acta* **49A** 303

[6] S Mohan and K G Ravikumar 1984 *Acta Phys. Polon.* **A 65** 557

[7] Schachtschneider 1986 *Vibrational Analysis of Polyatomic molecules*, Technical Report nos. **231-64** and **57-65** (Shell Development Co., Emeryville, California)

[8] S Mohan and R Murugan 1992 *Indian J. Pure Appl. Phys.* **30** 283

[9] L J Bellamy 1959 *The Infrared Spectra of Complex Molecules* (New York : John Wiley) p 70

[10] W R Augus, C K Ingold and A H Leckie 1936 *J. Chem. Soc* 925

[11] C R Bailey, R R Gordan and J B Hale 1946 *J. Chem. Soc.* 299

[12] H G Silver and J L Wood 1964 *Trans. Farad. Soc.* **60** 5

[13] E F Mooney 1964 *Spectrochim. Acta* **20** 1343

[14] S Pinchas, D Samuel and M Weiss-Broday 1961 *J. Chem. Soc.* 1688

[15] S Mohan, T J Bhoopathy and K G Ravikumar 1985 *Acta Phys. Polon.* **A67** 1133

[16] G Gunasekaran, S Mohan and Kalainathan 1988 *Acta Ciencia Indica* **XI V(P)** 77

[17] Vasuki and S Mohan 1990 *Indian J. Pure Appl. Phys.* **28** 200

[18] Hussein, Abdel-Shaty and K Howard 1977 *J. Mol. Struct.* **42** 37

[19] Yesook Kim and Katsunosuke Machida 1986 *Spectrochim. Acta* **42A** 881

[20] Shabbir Ahmad, Samuel Mathew and P K Verma 1982 *Indian J. Pure Appl. Phys.* **30** 764